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<b>(54) Title:</b> POWDER PAINT COMPOSITION		
<b>(57) Abstract</b>  The invention relates to a powder paint composition comprising a polymer containing endomethylene tetrahydrophthalic acid units, a crosslinker and a monophenolic compound, a bisphenolic compound and/or a polyphenolic compound. The phenolic compound may contain a t-butyl phenolic unit or a hydroquinone unit, for example, 2,6-di-t-butyl-p-cresol or 4,4'-butylidene bis (6-t-butyl-p-cresol).		

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POWDER PAINT COMPOSITION

5                   The invention relates to a powder paint composition comprising a binder composition containing a polymer that contains endomethylene tetrahydrophthalic acid units and a crosslinker.

                  WO98/46690 discloses a curable powder paint  
10 binder composition comprising a polymer containing endomethylene tetrahydrophthalic acid (HIMIC) units and a crosslinker. A powder coating obtained after curing of a powder paint containing this binder exhibits a colour b\* (measured with Dr. Lange CIELAB,  
15 DIN 6174, 1976) of 1.1, however the heatstability has to be improved. In case the paint is formulated in such a way that the heat stability is sufficient, the initial colour has to be improved.

                  It is the object of the present invention  
20 to provide a powder paint composition comprising a binder composition containing a polymer that contains endomethylene tetrahydrophthalic acid units and a crosslinker, resulting in an improved combination of  
the characteristics initial colour and heat stability.

25                   The powder paint composition according to the invention is characterized in that the composition comprises:

- a) a polymer containing endomethylene tetrahydrophthalic acid units,
- 30 b) a crosslinker and
- c) a monophenolic, a bisphenolic and/or a polyphenolic compound.

                  This non-airdrying powder paint composition results after curing in a powder coating having an  
35 improved combination of the characteristics colour and heat stability. Furthermore, the other desirable

properties such as for example impact resistance, flow and chemical resistance are obtained.

Preferably, the amount of component c) is less than 5 % by weight (relative to the total amount of a) and b)). More preferably this amount ranges between 0,05 and 3 wt.%.  
5

Suitable monophenolic compounds include for example, hydroquinone, hydroquinone monomethylether, 2,4-bis(1,1-dimethyl ethyl) phenol, methylhydroquinone, 2-t-butyl-hydroquinone, diamyl hydroquinone, 2-t-butyl-4-methylphenol, styrenated phenol, (1,1-dimethyl-ethyl)-4-methoxyphenol, 2,6-bis-(1,1-dimethyl-ethyl)-4-methylphenol, 2,6-di-t-butyl-4-ethyl-phenol, 2,6-di-t-butyl-4-(di-methyl-amino)-methylphenol, 2,6-di-butyl-4-sec-butylphenol, 2,6-di-butyl-4-nonyl-phenol, 2,4-dimethyl-6(-1-methyl-cyclohexyl)phenol, stearyl-3-(3',5''-di-t-butyl-4-hydroxyphenyl)propionate, 6-t-butyl-2,4-dimethylphenol, 2,6-di-t-butyl-4-n-butylphenol, 4-hydroxy-methyl-2,6-di-t-butylphenol, 2,6-di-t-butyl-p-cresol, 3, (3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, 2,4,6-tris-t-butylphenol and/or benzene propanoic-3-(1,1-dimethylether)-4-hydroxy-5-methyl-1,2-ethanediyl bis(oxy-2,1-ethanediyl)ester.  
10  
15  
20

Suitable bisphenolic compounds include for example 2,2'-methylene bis(6-t-butyl-4-methylphenol), 2,2'-methylene-bis(4-ethyl-6-t-butylphenol), 4,4'-butylidene bis(6-t-butyl-3-methylphenol), 2,2'-ethylidene(4,6-di-t-butylphenol), 2,2'-isobutylidene bis(4,6-dimethylphenol), 1,6-hexamethylene bis(3,5-di-t-butyl-4-hydroxyhydrocinnamate), 4,4' butylidene bis(6-t-butyl-m-cresol) and/or 2,4-bis-(1,1 dimethyl ethyl)phenol.  
25  
30

Suitable polyphenolic compounds include for example 1,1,3,-tris-(2-methyl-4-hydroxy-5-t-  
35

bytylphenyl)butane and/or pentaeritritol tetrakis(3,5-di-t-butyl-4-hydroxyhydrocinnamate).

According to a further preferred embodiment of the invention component c) is a component containing  
5 a t-butyl phenolic unit or a hydroquinone unit.

Preferred components containing a t-butyl phenolic unit are 2,6-di-t-butyl-p-cresol and 4,4'-butylidene bis (6-t-butyl-m-cresol).

The polymer a) generally contains at least  
10 10 wt.% and less than 100 wt.% (relative to the monomers), and preferably between about 35 and about 80 wt.% HIMIC. The HIMIC-units in the polymer a) act as functional acid end groups which may react with the crosslinker b).

15 The acid or hydroxyl functional polymer containing endomethylene tetrahydrophthalic acid units is preferably obtained by first preparing an unsaturated polymer which is subsequently reacted with cyclopentadiene (CPD) at a temperature between about  
20 160°C to about 220°C.

Preferably, the polymer prepared in the first step is an unsaturated polyester. This  
unsaturated polyester is generally formulated from one or more aliphatic and/or cycloaliphatic mono-, di-  
25 and/or polyvalent alcohols and one or more aliphatic, cycloaliphatic and/or aromatic di- or polyvalent carboxylic acids and/or esters derived therefrom. If desired also monocarboxylic acids may be applied.

Examples of suitable alcohols include  
30 benzyl alcohol, ethylene glycol, propylene glycol, neopentyl glycol, butane diol, hexane diol, dimethylol cyclohexane, diethylene glycol, glycerol, trimethylolpropane, pentaerythritol, dipentaerythritol, hydrated bisphenol-A, 2,2-bis-(2-hydroxyethoxy)phenylpropane

and/or 2,2-bis-2-hydroxypropoxy phenylpropane. Instead of or in addition to the alcohol compound(s) one or more epoxy compounds, such as for example ethylene oxide, propylene oxide and/or allylglycidyl ether or  
5 dicyclopentadiene may be used.

Examples of suitable di- or polyvalent carboxylic acids include maleic acid, fumaric acid, itaconic acid, citraconic acid, malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,4-  
10 cyclohexane dicarboxylic acid, hexahydrophthalic acid, hexachloro endomethylene tetrahydrophthalic acid, dichlorophthalic acid, isophthalic acid, terephthalic acid and/or trimellitic acid or esters thereof. The carboxylic acid can also be used in the form of an  
15 anhydride, for example tetrahydrophthalic anhydride, endomethylene tetrahydrophthalic anhydride, hexahydrophthalic anhydride, maleic anhydride or phthalic anhydride.

Optionally, saturated or unsaturated  
20 monocarboxylic acids, such as synthetic and/or natural fatty acids with 2 to 36 carbon atoms or esters prepared from these carboxylic acids and polyvalent alcohols such as glycerol may also be used. Examples of suitable monocarboxylic acids are lauric acid, stearic  
25 acid, oleic acid, linolic acid, benzoic acid, acrylic acid and/or methacrylic acid.

Preferably, the unsaturated polymer in the first step is an unsaturated polyester containing fumaric acid, maleic acid (anhydride) and/or  
30 terephthalic acid as acid units.

Preferably, the alcohol component of the unsaturated polyester is ethylene glycol, propylene glycol and/or neopentyl glycol.

The unsaturated polyester may be both  
35 crystalline and amorphous.

The amount of double bonds in the unsaturated polyester ranges usually between 120 and 2000 grams per unsaturated group and is preferably between 125 and 1500.

5           The molecular weight  $M_n$  (number average molecular weight) of the unsaturated polyester ranges usually between 500 and 6000, and is preferably between 1000 and 4500.

10           Acid functional polyesters usually have an acid number between 25 mg KOH/grams resin and 145 mg KOH/grams resin, preferably an acid number between 30 mg KOH/grams resin and 120 mg KOH/grams resin.

15           Hydroxyl-functional polyesters usually have a hydroxyl number between 25 mg KOH/grams resin and 145 mg KOH/grams resin, preferably a hydroxyl number between 30 mg KOH/grams resin and 120 mg KOH/grams resin.

The functionality is generally between 1.5 and 4 and is preferably between 1.9 and 3.5.

20           The preparation of the unsaturated polyester generally takes place in the presence of catalysts and inhibitors.

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Suitable catalysts include, for example, tetrabutyl titanate and dibutyl tin oxide.

25           Suitable inhibitors include, for example, butyl alcohol and t-butyl-hydroquinone.

The catalysts and inhibitors are generally used in amounts between 0.005 and 1 wt.% relative to the monomers.

30           The preparation of the unsaturated polyester may take place via a one-step process or via a multistep process.

35           If the unsaturated polyester preparation takes place via a one-step process, glycols, acids, catalysts and optionally inhibitors can be esterified

to the desired acid number or hydroxyl number at a temperature lower than 220°C. To remove low-molecular material or to obtain the desired acid number or hydroxyl number, optionally a vacuum can be applied at  
5 reduced temperature.

If the unsaturated polyester preparation takes place in two steps, in the first step saturated acids, glycols, catalysts and inhibitors can be esterified at temperatures between, for example, about  
10 210°C to about 260°C during for a period of about 2-10 hours, and in the second step the unsaturated compounds, acids and glycols can be esterified at temperatures between, for example, about 180°C to about 220°C for a period of about 5-16 hours. The monomers and  
15 the reaction conditions can be varied depending on the desired properties.

After the unsaturated polyester has been obtained dicyclopentadiene (DCPD) is added to the unsaturated polyester at temperatures between about  
20 160°C and about 220°C resulting in a retro Diels-Alder reaction forming CPD.

Next the cyclopentadiene (CPD) and the fumaric acid or maleic acid groups in the unsaturated polyester react by forming HIMIC-units. The amount of  
25 DCPD added is generally between 2 and 40 wt.% relative to the total weight of the monomers.

The functional acid or hydroxyl groups do not react during this reaction and may at a later stage, in the presence of a suitable crosslinker, cure  
30 to yield a powder coating.

The polymer that contains HIMIC units contains virtually no linear alkyl chains with more than 5 carbon atoms.

Since 1975 benzoin has virtually always



been used as the degassing agent in all types of powder paint compositions. This degassing agent must be included in the composition to expel the air or gas bubbles which became entrapped in the coating as the powder melts during the curing cycle. If gas bubbles were allowed to remain in the coating, the adhesion and protective effect of the coating would be impaired. A disadvantage of the use of benzoin is the brown coloration of powder coatings.

Preferably, the composition according to the invention contains less than 0,3% by weight (relative to the binder composition) of a degassing agent, preferably benzoine.

The preparation of thermosetting powder coatings in general and the chemical curing reactions of powder paints to form cured coatings are described by Misev in Powder Coatings, Chemistry and Technology (1991, John Wiley) on pp. 42-54, p. 148 and 224-226. A thermosetting binder composition is generally defined as the resinous part of the powder paint comprising a polymer and crosslinker.

~~Suitable crosslinkers include, for example,~~  
triglycidyl isocyanurate (TGIC), blocked isocyanates, amino resins, bisphenol-A epoxy resins, compounds containing  $\beta$ -hydroxyalkyl amide groups, and crosslinkers that contain epoxy groups and that have an aliphatic chain with 5-26 carbon atoms such as epoxidized oils, can be selected.

Preferably epoxy units containing crosslinkers, for example bisphenol-A-epoxy resin, are used.

The polymer: crosslinker weight ratio may be adjusted as necessary depending on the final use of the powder paint binder composition. It is also

possible to use a mixture of resins. The ratio between functional polymer groups : functional crosslinker groups can range, for example, between about 1:0.5 and 1:1.5.

5                   Component c) may be added during the synthesis of the polymer and during the powder paint preparation.

                  The powder paint binder composition and the powder paint system may, if desired, include customary  
10 additives such as, for example, pigments, fillers, degassing agents, flow agents and stabilizers.

                  Suitable pigments include without limitation inorganic pigments, such as for example titanium dioxide, zinc sulphide, iron oxide and  
15 chromium oxide, as well as organic pigments, such as for example azo compounds. Suitable fillers include, for example, metal oxides, silicates, carbonates and sulphates.

                  Suitable flow agents include for example,  
20 polyalkyl acrylates, fluorohydrocarbons and silicon oils. Other suitable additives include, for example, additives for improvement of the tribo-electric charging properties, such as sterically hindered tertiary amines, which are described in EP-B-371528.

25                   Powder paints according to the invention may be applied in the customary manner, for example by electrostatic spraying of the powder onto an earthed substrate and curing of the coating by exposure to heat at a suitable temperature during a sufficiently long  
30 period depending on for example the substrate. The powder applied can, for example, be heated in a gas oven, an electric furnace or by means of infrared radiation.

                  Thermosetting coatings from powder paint  
35 (coating) compositions for use in industrial

applications are further described in a general sense in Powder Coatings, Chemistry and Technology, Misev, pp. 141-173 (1991).

5 A composition according to the present invention may be used in a powder coating intended for use on metal, wood, paper or a plastic substrate. The preferred substrate is metal. Examples are general-purpose top coats for use in industry, equipment coatings and for example for cans, domestic and other  
10 small equipment. The coatings are also highly suitable in the automotive industry for coating of external and/or internal parts.

The invention will be further demonstrated with reference to the following, non-limiting examples.

15 In the following examples and experiments the characteristics are determined as follows:

- gel time: DIN 5599 Part B 200°C
- flow: visually
- reversed impact: ASTM-D2794/69
- 20 - colour: Dr. Lange CIELAB 1976  
DIN 6174
- gloss: ASTM D523/70
- heat stability: colour measurement of a coating  
with Dr. Lange CIELAB after a  
25 temperature treatment during a  
certain time.

The flow and the reversed impact are determined at a layer thickness of 50 µm.

30

Experiments I-IXPreparation of a HIMIC-containing polyester

A 3-litre reactor vessel with thermometer, stirrer and distillation set-up was filled with 620.7 g propylene glycol, 820.6 g terephthalic acid, 160.8 g trimethylol propane, 2.2 g dibutyltin oxide and 2.2 g triphenyl phosphite. After this, with a nitrogen stream being supplied for 8 hours, the temperature was raised to 225°C while water was distilled off. After the temperature of the distilled-off water had dropped to 80°C, the mixture was cooled to 160°C, after which 764.9 g fumaric acid and 0.1 g t-butyl hydroquinone were added. The temperature was then raised to 205°C in 9 hours. At an acid value of 115 mg KOH/g resin, cooling to 185°C took place and a vacuum was applied for 30 minutes.

Subsequently, the temperature was raised to 200°C and 435.2 g dicyclopentadiene was metered in an hour. The temperature was then kept at 180°C for half an hour, after which a vacuum was applied for half an hour.

A stabiliser in an amount as given in Table I was added and mixed for 15 minutes.

The polyester with 45 wt.% HIMIC was characterized by:

- acid number	78 mg KOH/g resin
- hydroxyl number	15 mg KOH/g resin
- viscosity	130 dPas (Emila, 165°C)
- glass transition temperature	57°C (Mettler, TA3000, 5°C/min.)

Table I

Exp.	amount	stabiliser
I	0.6 w%	mono-t-butyl hydroquinone
II	1.0 w%	4,4' butylidene bis (6-t-butyl-m-cresol)
III	0.5 w%	pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)
IV	1.0 w%	tri-ethylene-glycol-bis-3-(t-butyl-4-hydroxy-5-methyl-phenyl)-propionate
V	0.6 w%	hydroquinone monomethylether
VI	0.6 w%	hydroquinone
VII	1.0 w%	2,6-di-t-butyl-p-cresol
VIII	1.0 w%	2,4-dimethyl-6-(1-methylcyclohexyl)phenol
IX	2.0 w%	2,4-bis(1,1-dimethyl ethyl) phenol

Examples I-IX5 Powder paint preparation

A physical mixture consisting of 100 g of a polyester according to one of the Experiments I-IX, 100 g bisphenol-A-epoxy (Aradite GT7004™), 100 g titanium dioxide (Kronos 2310™), 3 g Resiflow-PV5™

10 (polyacrylate flow agent from Worlée), 0.4 g triphenyl methyl phosphoniumbromide and 1.5 g benzoin was first mixed in a premixer (Prism Premixer Lab 6) and then mixed in an extruder (Prism, TSE 16 PC). The extrudate was cooled, grounded and screened, yielding a powder

15 paint having a particle size of 90 µm. The powder paint was then electrostatically applied, in a layer thickness of about 70 µm, on a metal substrate and cured for 10 minutes at 200°C in an air circulation furnace.

20 The properties of all resulting powder paints and powder coatings were as follows:

- flow good
- reversed impact 160 inchpound

5 The initial colour b\* and the heat stability of the compositions comprising a polyester according to one of the Experiments I-IX are given in Table II.

10 Table II  
Coating properties

Polyester of Exp.	Initial colour b*	heat stability	
		$\Delta b^*$ 60'220°C	$\Delta b^*$ 10'240°C
I	1.5	3.5	1.4
II	1.4	3.6	2.5
III	2.2	1.5	0.9
IV	1.6	3.7	2.3
V	1.8	3.3	1.1
VI	2.4	2.3	1.1
VII	2.1	2.9	1.5
VIII	2.0	2.7	1.2
IX	2.0	2.7	1.8

15 The polyesters according to the Experiments I-IX result in powder coatings having a combination of good initial colour and a good heat stability.

#### Comparative Experiments A-I

20 Experiments I-IX were repeated with the only difference that stabilisers A-I (according to Table III) were applied instead of stabilisers used in I-IX.

Table III

Exp.	amount	Stabiliser
A		no stabilizer
B	2 w%	tris nonyl phenyl phosphite
C	2 w%	bis (2,4-di-t-butylphenyl)pentaerythritol diphosphite
D	2 w%	distearyl pentaerythritol diphosphite
E	2 w%	phenothiazine
F	2 w%	N,N',N'',N'''tetrakis(4,6 bis(butyl-(N-methyl 2,2,6,6 tetramethyl piperidine-4-yl)amino)triazine-2yl)4,7-diazadecane 1,10-diamine
G	2 w%	tris (2,4 di-tert butyl phenyl) phosphite
H	2 w%	di-octadecyl 3,3'thiodipropionate
I	2 w%	2,4 bis (2,4 dimethylphenyl)-6 (2 hydroxy-4-n-octyloxy phenyl) 1,3,5 triazine

Comparative Examples A-I

Examples I-IX were repeated with the use of the polyesters according to Experiments A-I (instead of the polyesters I-IX).

5

The coating properties, which were measured at a layer thickness of 150  $\mu\text{m}$ , are given in Table IV

Table IV

Exp.	b*	heat stability
		$\Delta b^* 60'220^{\circ}\text{C}$
A	6.7	10.7
B	6.8	11.0
C	7.7	11.2
D	6.3	11.3
E	6.4	10.0
F	6.9	10.5
G	6.9	9.6
H	6.5	9.5
I	7.9	10.7

10

A comparison between the Examples I-IX and the comparative examples shows that a composition comprising component c) results in a better combination of initial colour and heat stability than stabilisers A-I.

15

Experiment XPolyester preparation

20

A 3-litre reactor vessel with thermometer, stirrer and distillation set-up was filled with 620.7 g propylene glycol, 820.6 g terephthalic acid, 160.8 g trimethylol propane, 2.2 g dibutyltin oxide and 2.2 g



triphenyl phosphite. After this, with a nitrogen stream being supplied for 8 hours, the temperature was raised to 225°C while water was distilled off. After the temperature of the distilled-off water had dropped to 80°C, the mixture was cooled to 160°C, after which 764.9 g fumaric acid and 0.1 g t-butyl hydroquinone were added. The temperature was then raised to 205°C in 9 hours. At an acid value of 115 mg KOH/g resin, cooling to 185°C took place and a vacuum was applied for 1 hour. Subsequently, the temperature was raised to 200°C and 435.2 g dicyclopentadiene was metered in an hour. The temperature was then kept at 180°C for half an hour, after which a vacuum was applied for 45 minutes. 24.4 g 2,6-t-butyl-p-cresol was added and mixed for 15 minutes.

The polyester with 45 wt.% HIMIC was characterized by:

- |                                |                                  |
|--------------------------------|----------------------------------|
| - acid number                  | 78 mg KOH/g resin                |
| - hydroxyl number              | 20 mg KOH/g resin                |
| - viscosity                    | 183 dPas (Emila, 165°C)          |
| - glass transition temperature | 59°C (Mettler, TA3000, 5°C/min.) |

#### Example X

##### 25 Powder paint preparation

A physical mixture consisting of 100 g polyester according to Experiment X, 100 g bisphenol A epoxy (Aradite GT7004™), 100 g titanium dioxide (Kronos 2310™), 3 g Resiflow-PV5™ (polyacrylate flow agent from Worlée), 0.4 g triphenyl methyl phosphoniumbromide and 1.5 g benzoin was first mixed in a premixer (Prism Premixer Lab 6) and then mixed in an extruder (Prism, TSE 16 PC). The extrudate was cooled, grounded and

screened, yielding a powder paint having a particle size of 90  $\mu\text{m}$ . The powder paint was then electrostatically applied, in a layer thickness of about 70  $\mu\text{m}$ , on a metal substrate and cured for 10 minutes at 200°C in an air circulation furnace.

The properties of the resulting powder paint and powder coating were as follows:

	- flow	good
	- reversed impact	160 inchpound
10	- colour	L* 96.0
		a* -0.4
		b* 2.9
	- heat stability 60'220°C	$\Delta$ b* 2.9
	- heat stability 10'240°C	$\Delta$ b* 1.5
15	- degassing limit	118 $\mu\text{m}$

The degassing limit is the layer thickness at which coating imperfections, for example pinholes and cissing, caused by degassing can be seen.

20

#### Example XI

##### Powder paint preparation

Example X was repeated with the exception that 1.5 g benzoin was replaced by 0.6 g benzoin

The properties of the resulting powder paint and powder coating were as follows:

	- flow	good
	- reversed impact	160 inchpound
30	- colour	L* 97.0
		a* -0.4
		b* 1.3
	- heat stability 60'220°C	$\Delta$ b* 3.4

- heat stability 60'240°C                       $\Delta b^*$  1.9
- degassing limit                                      114  $\mu\text{m}$

5                      A comparison between Examples X and XI shows that by reducing the amount of benzoin the initial colour is improved while the degassing limit remains at the same level.

10    Comparative Experiment J

Preparation of a HIMIC-containing polyester

                    A 3-litre reactor vessel with thermometer, stirrer and distillation set-up was filled with 604.1 g propylene glycol, 820.6 g terephthalic acid, 160.8 g  
15 trimethylol propane, 0.05 wt.% dibutyltin oxide and 0.10 wt.% triphenyl phosphite. After this, with a nitrogen stream being supplied for 8 hours, the temperature was raised to 225°C while water was distilled off. After the temperature of the distilled-off water had dropped to  
20 80°C, the mixture was cooled to 160°C, after which 764.9 g fumaric acid and 1.1 g t-butyl hydroquinone were  
-----  
added. The temperature was then raised to 205°C in 9 hours. At an acid value of 138 mg KOH/g resin, cooling to 185°C took place and a vacuum was applied for 30  
25 minutes.

                    Subsequently, the temperature was raised to 200°C and 435.2 g dicyclopentadiene was metered in an hour. The temperature was then kept at 180°C for half an hour, after which a vacuum was applied for half an  
30 hour.

                    The polyester with 45 wt.% HIMIC was characterized by:

- acid number    81 mg KOH/g resin

- hydroxyl number 8 mg KOH/g resin
- viscosity 140 dPas (Emila, 165°C)
- glass transition temperature 61°C (Mettler, TA3000, 5°C/min.)

5

Comparative Example JPowder paint preparation

A physical mixture consisting of 100 g polyester according to Experiment J, 100 g bisphenol A epoxy (Aradite GT7004™), 100 g titanium dioxide (Kronos 2310™), 3 g Resiflow-PV5™ (polyacrylate flow agent from Worlée), 0.4 g triphenyl methyl phosphoniumbromide and 1.5 g benzoin was first mixed in a premixer (Prism Premixer Lab 6) and then mixed in an extruder (Prism, TSE 16 PC). The extrudate was cooled, ground and screened, yielding a powder paint having a particle size of 90 µm. The powder paint was then electrostatically applied, in a layer thickness of about 50 µm, on a metal substrate and cured for 10 minutes at 200°C in an air circulation furnace.

The properties of the resulting powder paint and powder coating were as follows:

- flow good
- reversed impact 160 inchpound
- 25 - colour L\* 95.0  
a\* -0.7  
b\* 1.1
- heat stability 60'220°C Δ b\* 5.0
- heat stability 10'240°C Δ b\* 2.5

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The powder paint binder composition comprising a polyester with 45% by weight HIMIC resulted in a powder coating with good flow properties

and in a light-coloured coating having an excellent reversed impact resistance. However, although the initial colour of the coating is excellent, the heat stability is insufficient.

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#### Comparative Experiment K

##### Preparation of a HIMIC-containing polyester

A 3-litre reactor vessel with thermometer, stirrer and distillation set-up was filled with 620.7 g propylene glycol, 820.6 g terephthalic acid, 160.8 g trimethylol propane, 2.2 g dibutyltin oxide and 2.2 g triphenyl phosphite. After this, with a nitrogen stream being supplied for 8 hours, the temperature was raised to 225°C while water was distilled off. After the temperature of the distilled-off water had dropped to 80°C, the mixture was cooled to 160°C, after which 764.9 g fumaric acid and 0.1 g t-butyl hydroquinone were added. The temperature was then raised to 205°C in 9 hours. At an acid value of 115 mg KOH/g resin, cooling to 185°C took place and a vacuum was applied for 30 minutes.

Subsequently, the temperature was raised to 200°C and 435.2 g dicyclopentadiene was metered in an hour. The temperature was then kept at 180°C for half an hour, after which a vacuum was applied for half an hour.

The polyester with 45 wt.% HIMIC was characterized by:

- |                                |                                  |
|--------------------------------|----------------------------------|
| - acid number                  | 78 mg KOH/g resin                |
| 30 - hydroxyl number           | 15 mg KOH/g resin                |
| - viscosity                    | 130 dPas (Emila, 165°C)          |
| - glass transition temperature | 57°C (Mettler, TA3000, 5°C/min.) |

Comparative Example KPowder paint preparation

A physical mixture consisting of 100 g polyester according to Experiment K, 100 g bisphenol A epoxy (Aradite GT7004™), 100 g titanium dioxide (Kronos 2310™), 3 g Resiflow-PV5™ (polyacrylate flow agent from Worlée), 0.4 g triphenyl methyl phosphoniumbromide and 1.5 g benzoin was first mixed in a premixer (Prism Premixer Lab 6) and then mixed in an extruder (Prism, TSE 16 PC). The extrudate was cooled, ground and screened, yielding a powder paint having a particle size of 90 µm. The powder paint was then electrostatically applied, in a layer thickness of about 70 µm, on a metal substrate and cured for 10 minutes at 200°C in an air circulation furnace.

The properties of the resulting powder paint and powder coating were as follows:

- flow	good
- reversed impact	160 inchpound
- colour	L* 95.0
	a* -0.5
	b* 4.4
- heat stability 60'220°C	Δ b* 2.3
- heat stability 10'240°C	Δ b* 1.4

The powder paint binder composition comprising a polyester with 45% by weight HIMIC resulted in a powder coating with good flow properties, having an excellent reversed impact resistance and a sufficient heat stability. However, the initial colour of the coating was insufficient.

C L A I M S

1. A powder paint composition comprising
- 5 a) a polymer containing endomethylene tetrahydrophthalic acid units,
- b) a crosslinker and
- c) a monophenolic compound, a bisphenolic compound and/or a polyphenolic compound.
2. A composition according to Claim 1 characterised
- 10 in that the monophenolic compound is hydroquinone, hydroquinone monomethylether, 2,4-bis(1,1-dimethyl ethyl) phenol, methylhydroquinone, 2-t-butyl-hydroquinone, diamyl hydroquinone, 2-t-butyl-4-methylphenol,
- 15 styrenated phenol, (1,1-dimethyl-ethyl)-4-methoxyphenol, 2,6-bis-(1,1-dimethyl-ethyl)-4-methylphenol, 2,6-di-t-butyl-4-ethyl-phenol, 2,6-di-t-butyl-4-(di-methyl-amino)-methylphenol, 2,6-di-butyl-4-sec-butylphenol, 2,6-di-butyl-4-nonyl-
- 20 phenol, 2,4-dimethyl-6(-1-methyl-cyclohexyl)phenol, stearyl-3-(3',5''-di-t-butyl-4-hydroxyphenyl)propionate, 6-t-butyl-2,4-dimethylphenol, 2,6-di-t-butyl-4-n-butylphenol, 4-hydroxy-methyl-2,6-di-t-butylphenol, 2,6-di-t-butyl-p-cresol, 3, (3,5-di-tert-butyl-4-
- 25 hydroxyphenyl)propionic acid, 2,4,6-tris-t-butylphenol and/or benzene propanoic-3-(1,1-dimethylether)-4-hydroxy-5-methyl-1,2-ethanediyl bis(oxy-2,1-ethanediyl)ester.
- 30 3. A composition according to Claim 1 characterised in that the bisphenolic compound is 2,2'-methylenebis(6-t-butyl-4-methylphenol), 2,2'-methylene-bis(4-ethyl-6-t-butylphenol), 4,4'-butylidene bis(6-t-butyl-3-methylphenol), 4,4'
- 35 butylidene bis (6-t-butyl-m-cresol),

- 2,2'-ethylidene(4,6-di-t-butylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol) 1,6-hexamethylenebis(3,5-di-t-butyl-4-hydroxyhydrocinnamate) and/or 2,4-bis-(1,1 dimethyl ethyl)phenol.
- 5
4. A composition according to Claim 1, characterised in that the polyphenolic compound is 1,1,3,-tris-(2-methyl-4-hydroxy-5-t-butylphenyl)butane and/or pentaerythritol tetrakis(3,5-di-t-butyl-4-
- 10 hydroxyhydrocinnamate).
5. A composition according to any one of Claims 1-4, characterized in that the phenolic compound contains a t-butyl phenolic unit or a hydroquinone unit.
- 15 6. A composition according to any one of Claims 1-5, characterized in that the phenolic compound is 2,6-di-t-butyl-p-cresol or 4,4' butylidene bis (6-t-butyl-m-cresol).
7. A composition according to any one of Claims 1-6,
- 20 characterized in that the crosslinker is an epoxy unit containing crosslinker.
8. A composition according to any one of Claims 1-7, characterized in that the composition comprises less than 0,3% by weight of a degassing agent.
- 25 9. A powder paint composition according to any one of Claims 1-8 and optionally pigment, catalyst, fillers and additives.
10. A powder coating obtained after curing of a powder paint composition according to any one of
- 30 Claims 1-9.
11. A wholly or partly coated substrate, characterized in that as coating a powder coating according to Claim 10 has been used.



## INTERNATIONAL SEARCH REPORT

International application No

PCT/NL 00/00274

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09D167/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 46690 A (BELDER EIMBERT GERRIT ;KOLDIJK FOKELTJE AKKE (NL); MISEV TOSKO ALE) 22 October 1998 (1998-10-22) cited in the application page 7, line 30 -page 8, line 2; claims 1-10	1-11
Y	GB 1 090 265 A (EASTMAN KODAK COMPANY) page 3, line 13 -page 7, line 15	1-11
A	DE 10 59 598 B (PITTSBURGH PLATE GLASS COMPANY) claims 1-4	1,2
A	FR 2 200 296 A (HUELS CHEMISCHE WERKE AG) 19 April 1974 (1974-04-19) claims 1,2	1,2

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internatio. application No  
PCT/NL 00/00274

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9846690 A	22-10-1998	NL 1005809 C AU 9243398 A EP 0975703 A	19-10-1998 24-11-1998 02-02-2000
GB 1090265 A		NONE	
DE 1059598 B		NONE	
FR 2200296 A	19-04-1974	DE 2246819 A CH 586729 A GB 1437043 A IT 996195 B NL 7313064 A,B	25-04-1974 15-04-1977 26-05-1976 10-12-1975 26-03-1974